### APPENDIX G

## DEVELOPMENT OF SITE-SPECIFIC WATER QUALITY CRITERIA: A CASE STUDY USING THE RESIDENT SPECIES PROCEDURE

Here we describe the development of site-specific water quality criteria using USEPA's Resident Species procedure for copper in Blaine Creek, Kentucky (KCPo and AEPSC 1992, Dobbs *et al.* 1994) to identify critical steps in the creation of site-specific water quality criteria and discuss relevant issues that arise during the process.

### **JUSTIFICATION**

The operation permit for Big Sandy Power Plant limited maximum concentrations of total recoverable copper in the plant's effluent. Big Sandy is a coal-fired power plant managed by Kentucky Power Company (KPCo) and American Electric Power Service Corporation (AEPSC). Fly ash produced during coal combustion is sluiced to a 44 ha settling pond, where physical and chemical treatment of the ash slurry occurs. A tower discharge structure equipped with a skimmer allows overflow from the pond into a 190 m effluent ditch that discharges to Blaine Creek. Based on analysis of outfall data, KPCo determined that compliance with these limits was not possible. KPCo and AEPSC then requested permission from the Kentucky Department for Environmental Protection to develop a copper site-specific water quality criterion for a segment of Blaine Creek.

Site-specific criteria recognize that the physical, chemical, and biological conditions at a site can influence the toxicity of a substance to aquatic organisms. These conditions vary among sites, and may be significantly different from those in which national and statewide criteria were developed. A copper site-specific criterion was appropriate for Blaine Creek because the recommended national and statewide criterion protects sensitive species that are not present in this stream, and laboratory tests from which the recommended national and statewide criterion were computed exposed organisms to dissolved forms of these chemicals. Often, only small fractions of the total concentrations of copper in effluents from a power plant are soluble. Furthermore, analysis of biological data collected by KPCo for several years suggested that the fly ash pond discharge had no deleterious effects on aquatic life use in Blaine Creek (KPCo and AEPSC, 1992; Van Hassel et al., 1988). In fact, the presence of fly ash pond discharge actually maintained the aquatic life use during critical (low flow) conditions prior to flow regulation at Yatesville Dam. Approval and adoption of the proposed site-specific criterion would allow KPCo to continue to discharge treated fly ash without costly alternative technologies. Such technologies would require initial capital investments in the range of 2.6 to 31 million dollars, and would not provide measurable benefits to the Blaine Creek biota since water use classifications were being maintained without them.

#### STUDY AREA

Blaine Creek is a fifth-order tributary to the Big Sandy River, located in eastern Kentucky. The Blaine Creek watershed covers an area of 686 km<sup>2</sup> and lies in the Western Allegheny Plateau ecoregion, which is characterized as having low to high hills, mixed mesophytic forest, and alfisol-type soils (Omernik, 1987). Blaine Creek receives treated fly ash water from KPCo Big Sandy power plant about 3.2 km upstream of the Big Sandy River confluence. The Big Sandy

Page G-2

power plant is coal-fired, and its two units have a combined generating capacity of 1,060 megawatts (MW). Fly ash produced during the coal combustion process is sluiced to a 44 hectares settling pond that discharges into Blaine Creek. At the time this study was undertaken, the discharge contributed <10 percent of the creek's flow. Historically, the discharge has comprised as much as 75 percent of creek flow during low flow conditions. In 1991, Blaine Creek was impounded by a U.S. Army Corps of Engineers dam located near Yatesville, Kentucky. Because of this flow regulation, the fly ash discharge would make up no more than 33 percent of total stream flow under worst-case conditions (stream low flow and effluent maximum design flow).

### Copper Speciation

The fraction of dissolved copper in Blaine Creek water downstream of the fly ash pond discharge was used as an estimate of bioavailable copper. Analyses of total recoverable and dissolved copper were performed on samples from the discharge and Blaine Creek during 1990 and 1991. Total recoverable copper was determined using USEPA methods 220.2 or 200.7 (Kopp and Mckee, 1983). Dissolved copper was determined by filtration through a 0.45  $\mu$ m filter at the time of collection, followed by acidification with HNO<sub>3</sub> (0.5 percent). Analysis of the preserved samples was similar to USEPA method 220.2, but without a digestion step. The ratio of dissolved to total recoverable copper was used to adjust the final criterion value in terms of bioavailable copper.

The geometric mean ratio of dissolved to total recoverable copper in the discharge from 1990 to 1991 was 0.77 and indicated that approximately three-quarters of the copper was in bioavailable form (Table 1). There was a distinct difference between the two years. During 1990, the geometric mean of the ratio was 0.67 for the discharge; in 1991, copper was almost completely in the dissolved form with the geometric mean ratio of 0.90. This difference in the relative amount of dissolved copper may be attributed to climate factors and decreasing suspended solid levels in the discharge. Very wet conditions prevailed in 1990 (causing substantial stormwater runoff into the fly ash pond), whereas drought conditions were evident in 1991.

Table 1. COPPER SPECIATION STUDY OF BIG SANDY PLANT ASH POND DISCHARGE AND BLAINE CREEK SAMPLES DOWNSTREAM OF DISCHARGE (μG/L), 1990 AND 1991

_	Outfall			Blaine	Blaine Creek Below Outfall			
Date	Total	Dissolved	$Ratio^a$	Total	Dissolved	Ratio <sup>a</sup>		
7 Jul 90	23	14	0.61	4	3	0.75		
17 Jul 90	23	18	0.78	6	_b	-		
19 Jul 90	23	18	0.78	6	_b	-		
24 Jul 90	12	11	0.92	5	3	0.60		
31 Jul 90	19	12	0.63	5	4	0.80		
7 Aug 90	13	14	1.0	4	3	0.75		
14 Aug 90	23	3	0.13	6	5	0.83		
21 Aug 90	8	_b	-	10	6	0.60		
28 Aug 90	31	12	0.39	13	4	0.31		
4 Sep 90	15	14	0.93	15	6	0.40		
9 Sep 90	_b	_b	-	4	2	0.50		
11 Sep 90	11	8	0.73	5	9	1.0		
18 Sep 90	6	6	1.0	4	_b	-		
24 Oct 91	4	3	0.75	2	1	0.5		
29 Oct 91	6	6	1.0	3	3	1.0		
5 Nov 91	20	20	1.0	7	5	0.71		
12 Nov 91	24	25	1.0	8	7	0.88		
18 Nov 91	24	27	1.0	5	5	1.0		
25 Nov 91	19	21	1.0	7	5	0.71		
5 Dec 91	24	23	0.93	5	1	0.20		
9 Dec 91	28	30	1.0	10	2	0.20		
16 Dec 91	42	25	060	4	2	0.50		
23 Dec 91	43	35	0.81	4	2	0.50		
Geometric Mean	17	14	0.77	6	3	0.58		

The ratio is equal to the dissolved copper levels divided by the total recoverable value. All analyses based on split samples.

For regulatory purposes, the samples of concern are from the downstream site after complete mixing of Blaine Creek and the discharge. The geometric mean dissolved-to-total-copper ratio for the 1990 samples (n = 10) was 0.62: for the 1991 samples (n = 10), it was 0.54. When the two studies were pooled, the geometric mean of the ratio for all samples (n = 20) was 0.58. These

<sup>&</sup>lt;sup>a</sup> For samples in which the dissolved copper was greater than total copper the ratio was set equal to one.

<sup>&</sup>lt;sup>b</sup> Sample lost due to contamination or not taken.

results suggest that a substantial fraction of the copper in Blaine Creek below the fly ash pond discharge was not in a highly bioavailable form. Considering the importance of copper speciation in regulating toxicity, application of criteria based on total recoverable copper levels may be over protective. Adequate protection to aquatic life in Blaine Creek would require adjustment of the national FAV with the geometric mean ratio of dissolved to total recoverable copper (from the fully mixed downstream location).

### Toxicity Tests – Materials and Methods

Acute toxicity tests were performed on nine species that reside in Blaine Creek to determine 48-hours LC<sub>50</sub> values for copper. These organisms fulfilled all requirements of the national guideline procedures (Stephan et al., 1985). Integration of results was based on the USEPA's resident-species procedure (USEPA, 1983; Carlson et al., 1984).

Blaine Creek water was used as dilution water for all tests and was collected 10 km upstream of the discharge, near Fallsburg, Kentucky, in 19 L polycarbonate carboys and stored at room temperature for a period not exceeding 14 days before use. The water was filtered (1.6  $\mu$ m) due to high levels of suspended solids during initial water collection trips. During the study, Blaine Creek was typified by highly variable flow due to stream terrain of the watershed, which causes frequent flooding with associated elevated levels of suspended solids. The decision to filter the water for all tests was made to provide dilution water with more consistent characteristics because of the effect that suspended solids have on copper bioavailability.

Species used for toxicity testing were selected on the basis of potential residency in the Blaine Creek watershed, fulfillment of the national guidelines selection criteria (Stephan et al., 1985), state requirements, and availability of the tests organisms of a suitable age. Residency of a species was based on long-term fish and macroinvertebrate biosurvey data from various stream sites (KPCo and AEPSC 1992, Van Hassel et al., 1988). The only organism that was originally sought but could not be found in sufficient quantity was the bluntnose minnow (*Pimephales notatus*). The fathead minnow (*P. promelas*) was used as a surrogate species. Nine different species were tested to fulfill the national guidelines requirement (Stephan et al., 1985) for eight species in selected families and the state of Kentucky's requirements for a species from a coppersensitive family (Daphnidae).

The following organisms were obtained from either house cultures or commercial sources: Daphnia pulex, P. promelas, Lepomis macrochirus, Physella sp. and Chronomus riparius. The salamander Eurycea bislineata, crayfish Orconcectes sp., and mayflies Stenonema sp. and Isonychia bicolor were collected from locales where their relative population abundance and condition were known from prior collection experience. After collection and transportation of organisms to the lab in coolers that had been chilled to the collection temperature, the organisms were allowed to acclimate to Blaine Creek water for a minimum of 48 hours. Temperature acclimation of test organisms was not a major concern in this study because collection sites remained within 2° of 20°C over the course of the study. The period of acclimation was an acceptable balance between allowing the organisms to recover from the stress of the handling and the potential problem of reduced health after long-term holding.

Acute toxicity tests lasted 48 hours and used 1.6 um filtered Blaine Creek water as the dilution water. All tests were conducted at 20°C with 16:8 light:dark photoperiod. Standard conditions were three replicate test containers containing 10 organisms each, with five concentrations and a control for each test. Method development before performing definitive tests consisted of a series

of screening tests with each species to optimize holding conditions and test parameters for nonstandard species. This design was essential for performing valid toxicity tests. Testing methods generally followed those outlined by Weber (1991) and Standard Methods for the Examination of Water and Wastewater (APHA et. al., 1985). The screening tests resulted in selection of optimal test concentrations, which led to narrower confidence intervals. Samples for total recoverable copper determination were taken at the beginning and end of the test and analyzed in accordance with USEPA method 2007 (Kopp and Mckee, 1983). Species-specific conditions are described below.

Testing of *D. pulex* and *P. promelas* followed closely the protocols described by Weber (1991), except three replicates (instead of two) of 10 organisms each were used and the test duration for both organisms was 48 hours. *Daphnia pulex* were cultured in filtered Baine Creek water for at least one month before testing. Neonates were < 24 hours hold at test initiation and were tested in 100 ml Pyrex<sup>®</sup> beakers containing 50 ml test solution.

Three-week-old *P. promelas* from in-house cultures were tested in 1 L glass beakers with 750 ml test solution. The minnows were reared in dechlorinated tap water (treated New River, VA water) and transferred to Blaine Creek water one week before testing. Juvenile *L. macrochirus* (35 mm length) were obtained from Kurtz Fish Hatchery (Elverson, PA) and were acclimated for one week in Blaine Creek water. The average wet weight at the time of testing was 0.51 gram per fish. Fish were tested in 17 L polycarbonate vessels containing 7 L test solution for 48 hour.

The two-lined salamander, *E. bislineara*, was collected from an unnamed tributary to Little Scary Creek (near Winfield, WV) and transported to the lab in coolers chilled at 20°C. Organisms were acclimated before use to Blaine Creek water for 2 days without feeding. Salamanders (average length 40 mm) were tested in covered 17 L polycarbonate vessels containing 6 L tests solution. An equal number of washed stones of similar size (10-20 cm maximum diameter) were placed in each container to provide refugia.

Crayfish (*Orconectes* sp.) were collected from Sinking Creek (Newport, VA) and transported in chilled coolers. Crayfish were acclimated for 48 hours in Blaine Creek water before testing. Low dissolved oxygen (DO) in screening tests necessitated gently aerating 5 L tests solution with Pasteur pipettes in 17 L polycarbonate vessels. Crayfish (30-40 mm in length) were used in the tests and were checked for exoskeleton condition before use.

Mayflies (sixth-to-eighth-instar *Stenonema* sp. and *I. bicolor*) were collected from Sinking Creek and acclimated for 48 hours to Blaine Creek water before use. Mayflies were tested in 2 L Nalgene® (Rochester, NY) containers washed cobble added to provide substrate. Current was provided by a stir bar positioned over a magnetic stir plate in the center of the container. Stir-bar speed was determined from trial and error before conducting the definitive tests.

Physella sp. (<10 mm diameter) were obtained from in-house cultures at Virginia Tech (Blacksburg, VA) and acclimated in Blaine Creek water for 48 hours before use. They were tested in loosely covered 350 ml glass culture dishes filled to within 1.5 cm of the top with test solution to prevent the snails from avoiding the toxicant. Snails were considered dead after 48 hours if no movement of the foot or antenna was evident in the test solution after being placed in control water for 5 minutes

*Chironomus riparius* was obtained from in-house cultures at Virginia Tech and acclimated to Blaine Creek water for 48 hours. Second instar midges were tested in 350 ml glass culture dishes using 250 ml test solution and 10 ml of glass beads (150-300  $\mu$ m) as inert substrate.

DO, pH, and temperature were monitored daily at all concentrations when a sufficient volume was available. Alkalinity and hardness were measured at the beginning and the end of the tests in the control and the highest level. Water samples (50 ml) were collected at the surface of the containers from all treatment levels at the beginning and end of the tests. The samples were preserved with 150  $\mu$ l of 50 percent HNO<sub>3</sub> and shipped to a commercial lab for total recoverable copper analysis by USEPA method 200.7 (Kopp and Mckee, 1983).

The trimmed Spearman-Karber method (Hamilton et al.,1977) was used to calculate 48 hours median lethal concentrations and respective 95 percent confidence intervals. Total recoverable copper measurements taken at the beginnings of the tests were used for calculation of  $LC_{50}$  values.

Integration of test results was conducted using USEPA's FAV equation (Stephan et al., 1985, Erickson and Stephan, 1988). The FAV equation is an extrapolation procedure that plots the log of the acute values against the cumulative probability of the relative sensitivity of the species in the database to the chemical. The cumulative probability of a species is determined by dividing the rank of each acute value by the total sample size in the database plus one. The FAV is the concentration that corresponds to a 0.5 cumulative probability level estimated by using the best-fit line through the four acute values closest to the 0.05 level. At the 0.05 level, 95 percent of the species in the statistical population that the database represents will be less sensitive, whereas 5 percent will be more sensitive. This procedure is designed to protect 95 percent of the species within the entire database. To obtain the CMC, the FAV is divided by two. For the purposes of this study, the criterion continuous concentration (CCC) was derived by dividing the site-specific FAV by the ACR of 2.823 from national criteria document (USEPA 1984).

### Toxicity Tests – Results and Discussions

Based on the results of the nine definitive acute toxicity tests, D. pulex was the most sensitive taxon tested, with a LC<sub>50</sub> of 17  $\mu$ g/L Cu (Table 2). This finding is consistent with the USEPA database (USEPA, 1984), which lists species in the family Daphnidae among the least tolerant taxa. The four most sensitive species in the Blaine Creek database were from a broad range of taxonomic groups and included *Physella* sp. (LC<sub>50</sub> 109  $\mu$ g/L).

TABLE 2. RESULTS OF ACUTE TOXICITY TESTS WITH COPPER USING DILUTION WATER FROM BLAINE CREEK.

Rank	Species	LC <sub>50</sub> (μg/L)	95 percent Confidence limits
1	Daphnia pulex (water flea)	37	35-38
2	Physella sp. (snail)	109	100-118
3	Isonychia bicolor (mayfly)	223	162-109
4	Pimephales promelas (fathead minnow)	283	242-334
5	Stenonema sp. (mayfly)	453	372-551
6	Eurycea bislineata (salamander)	1,120	872-1,450
7	Chironomus riparius (midge)	1,170	946-1,450
8	Orconectes sp. (crayfish)	2,370	1,830-3,070
9	Lepomis macrochirus (bluegill sunfish)	4,300	3,350-5,520

All tests were conducted at hardness values between 100 and 120 mg/L as CaCO<sub>3</sub>

To compare the LC<sub>50</sub> values from Blaine Creek database directly with those of similar species as reported in the national criteria document (USEPA,1984), values were normalized to a hardness of 50 mg/L as CaCO<sub>3</sub>, based on the following equation (USEPA, 1984):

 $LC_{50}$  at hardness of  $50 = e^{Y}$ 

 $Y = [\ln (LC_{50}) - 0.9422 (\ln (test hardness) - \ln (50)]$ 

where: 0.9422 is the pooled slope between hardness and LC<sub>50</sub> values for all species in the USEPA database.

The two databases have a similar ranking of species sensitivity (Table 3). The hardness-adjusted LC<sub>50</sub> value for D. pulex (17.3  $\mu$ g/L) in Blaine Creek water is lower than the species mean acute value (25.42  $\mu$ g/L) reported by the USEPA. However, the GMAV for *Daphnia* (17.08  $\mu$ g/L), used by USEPA to calculate the FAV, was almost identical to the previously recorded value. The response of 51.0  $\mu$ g/L for the snail (*Physella* sp.) is quite similar to that of 39.33  $\mu$ g/L for *Physa*, which is the most sensitive snail in the USEPA database. The acute values for both the fathead minnow (*P. promelas*) and the crayfish (*Orconectes* sp.) are in close agreement with the two databases. No comparisons were possible for the two mayflies and the salamander tested because the USEPA database does not contain any similar species.

TABLE 3. COMPARISON OF THE BLAINE CREEK AND USEPA (USEPA, 1984) ACUTE DATABASE FOR COPPER

	$LC_{5O}$ (µg/L)			
Test species	Blaine Creek	USEPA		
Daphnia pulex	17.3	25.42		
Daphnia	-	17.08		
Physella sp.	51.0	-		
Physa	-	39.33		
Isonychia bicolor	109	-		
Pimephales promelas	133	115.5		
Pimephales	-	91.29		
Stenonema sp.	212	-		
Eurycea bislineata	524	-		
Chironomus	547	76.92		
Orconectes	1,110	1,397		
Lepomis macrochirus	2,010	1,017		

All acute values were standardized to a hardness of 50 mg/L as CaCO.

There were discrepancies between the two databases for species that were less sensitive to copper. The LC<sub>50</sub> value of 547  $\mu$ g/L for *Chironomus* is appreciably higher than the GMAV of 76.92  $\mu$ g/L reported by USEPA. This difference may be due to the use of different species of *Chironomus* and/or different test procedures. The LC<sub>50</sub> value for bluegill sunfish was twice as high than reported by USEPA and may be due to the effect of site water on the bioavailability of copper at higher test concentrations. A blueish-white precipitate was observed at higher test concentrations (> 1,000  $\mu$ g/L nominal), and the quantity appeared to increase with dose, indicating loss of copper from the test solution. The precipitate formed relatively rapidly and was evident at the higher test levels within hours. The observation that the bioavailability of a metal changes during the exposure period was also reported by Parkerton and colleagues (Parkerton et al., 1988) who found that the toxicity of zinc is reduced by predosing site water 24 hours before exposure of test organisms.

Water quality parameters were similar for all toxicity tests; typical values for the dilution water were hardness, 100 - 120 mg/L as CaCO<sub>3</sub>,; alkalinity, 50 - 60 mg/L as CaCO<sub>3</sub>,: pH, 7.5 - 7.8 DO levels were within 80 percent of saturation for all tests. Because the fly ash pond discharge caused a substantial increase in the hardness of the water downstream (i.e., 100-173 mg/L as CaCO<sub>3</sub> after addition of an effluent at 326 mg/L), the dilution water hardness was lower downstream of the discharge after complete mixing.

In conducting the necessary acute toxicity tests, a number of practical decisions affect the relevance of the resident species procedure in accounting for the site-specific factors that may modify chemical toxicity. The first decision that affects the results is species selection. Although species selection guidelines are relatively broad (Stephan et al., 1985), the actual species selected are based on practical considerations. The availability of test organisms usually is a key factor in the selection process. Ideally, tests organisms should be from the system being studied. Because this process can be difficult and have a negative impact on the ecosystem, representative

organisms from a variety of sources are used. This typically leads to reliance on standard test species as much as possible. Although the selected species should represent ecologically important species covering a full range of sensitivity to the chemical of interest, the reliance on standard test organisms can lead to a prevalence toward the use of more sensitive species. The more representative the tests species are of the ecosystem being protected, the more accurate the resulting criteria will be for protecting aquatic life in a specific ecosystem. A site-specific-criteria demonstration should not, by its very design, be subject to overprotective assumptions that often characterize national criteria.

In addition to differences in species composition between a site and the national database, the resident species procedure is designed to account for the effect of site water on chemical toxicity. The USEPA site-specific guidance suggests collection of dilution water from a pristine site for use as dilutent (USEPA, 1984). In this study, water was collected 10 km upstream of the discharge because of limited river access and concern for nonpoint sources of pollution directly above the discharge. Because the effluent substantially changed the chemical characteristics of the creek under low flow conditions (at least historically), the water used for toxicity testing was probably not representative of downstream conditions. Collection of water below the discharge, after complete mixing, would more accurately reflect the effect of site water in the area of concern. The authors support the recent change in the USEPA site-specific guidelines that recommends using water from downstream of any potential pollutant sources, after all are well mixed with the receiving system (USEPA, 1992). Additional factors that can affect the relevance of the procedure are site water availability, whether the water is filtered, and water storage conditions.

### Criteria Derivation and Evaluation

As discussed earlier, a number of alternative procedures are available to derive WQC. Based on the information available from Blaine Creek, three alternatives to derive site-specific WQC for copper are possible: (a) recalculation procedure, (b) resident-species procedure, and (c) recalculation modified by copper speciation data. These three alternatives result in distinctly different criteria that are summarized in Table 4. Choice of the most appropriate procedures should be driven by an evaluation of site-specific factors that are most important in a specific situation and should be considered the total sum of data available for a site.

### Table 4. CALCULATION OF THE CONTINUOUS MAXIMUM CRITERION (CMC) FOR COPPER, APPLICABLE TO BLAINE

# CREEK USING DIFFERENT PROCEDURES AT A HARDNESS OF 50 MG/L (UNLESS OTHERWISE NOTED, EXPRESSED IN TERMS OF $\mu$ G/L CU)

Criterion derivation procedure	Database size	FAV <sup>a</sup>	CMC	CMC at hardness 173 mg/L
National	41	18.5	9.23	29.7
Site-specific				
Recalculation	33	19.4	9.68	31.2
Recalculation with metal speciation	33	33.4	16.7	53.8
Resident species	9	10.1	5.1	16.2
Resident species <sup>b</sup>	33	36.3	18.1	58.4

<sup>&</sup>lt;sup>a</sup> Final acute value.

### Recalculation Procedure

The first step to determine if a site-specific WQC study is necessary should be recalculation of the FAV. The recalculation procedure entails no lab or fieldwork, as nonresident species are removed from the national criteria database and the FAV is recalculated (USEPA 1983, Carlson et al. 1984). Because this procedure is designed to correct for differences in species composition between the national database and a specific site, it is an inexpensive method to determine if differences in species composition are a prominent factor for a specific situation. For Blaine Creek, the recalculation procedure involves mainly removing non-indigenous coldwater species such as the northern squawfish from the national database. The recalculation procedure (n = 33) results in a FAV of 19.4  $\mu$ g/L at a hardness of 50  $\mu$ g/L (Table 4). This is slightly higher than the national value (18.5  $\mu$ g/L), indicating only a slight difference in species sensitivity after nonresident species are excluded. The CMC, using the mixed downstream site hardness, would be 31.2  $\mu$ g Cu/L (Table 4). Although this procedure can address whether differences in species composition is a factor, it does not address whether there is a site-water effect. Based on the results of the recalculation procedure, additional work using a procedure that considers site-water effects would be recommended.

### Resident Species

After generating LC<sub>50</sub>s for the nine species in the database, the next step was to integrate this information using the FAV equation. The site-specific FAV based on the Blaine Creek database (n = 9) was estimated as 22.0  $\mu$ g/L Cu. At the mean test hardness of 112 mg CaCO<sub>3</sub>/L, the FAV was assessed as 10.1  $\mu$ g/L Cu. This is less than two-thirds of the national FAV of 18.5  $\mu$ g/L at a hardness of 50 mg/L. At the downstream hardness of 173 mg/L as CaCO<sub>3</sub>, the resulting CMC is 16.4 and the CCC is 11.5  $\mu$ g/L compared to the statewide values of 29.7 and 21.1  $\mu$ g/L, respectively. This result was unexpected because LC<sub>50</sub> values for similar species in both databases were generally within a factor of two (Table 3) and because the lowest acute value used to calculate the FAV was almost identical (Table 5). The results of the calculation process erroneously imply that the Blaine Creek database represents a more sensitive ecosystem than the

<sup>&</sup>lt;sup>b</sup> Example of the role database size has in calculating FAV.

national database, yet the species-by-species comparison of the two databases does not support this conclusion. Furthermore, low values of the calculated criteria are not consistent with long-term biosurvey data from Blaine Creek, which show the designated aquatic life use being supported (KPCo and AEPSC, 1992). Van Hassel and collaborators (1988) found no statistical correlations between macroinvertebrate taxa richness and measured in-stream concentrations of several toxic metals, including copper.

Table 5. COMPARISON OF LOWEST FOUR ACUTE VALUES USING THE RESIDENT SPECIES AND RECALCULATION PROCEDURES FOR BLAINE CREEK (ALL VALUES ADJUSTED TO A HARDNESS OF 50 MG/L AS CACO<sub>3</sub>).

Resident species $(n = 9)$			Recalculation $(n = 33)$			
Cumulative Probability	Genus	$GMAVs^{a}$	Cumulative Probability	Genus	GMAVs	
0.10	Daphnia	17.3	0.03	Daphnia	17.08	
0.20	Physella	51.0	0.06	Ceriodaphnia	18.77	
0.30	Isonychia	109	0.09	Gammarus	25.22	
0.40	Pimephales	133	0.12	Plumatella	17.05	

<sup>&</sup>lt;sup>a</sup> Genus mean acute values.

The resident species values are the four lowest in the Blaine Creek site-specific database. The recalculation procedure values are the four lowest in the USEPA national database.

An evaluation of the criteria derivation process indicates that the low FAV for copper in Blaine Creek using the resident species procedure is a function of the calculation process and does not represent a site-water effect or true differences in species sensitivity. The controlling factor appears to be the effect of database size in derivation of the FAV. Although previous investigators (Spehar and Carlson 1984, USEPA 1983, Carlson et al., 1984) have mentioned the role of database size on the FAV, they failed to recognize the extreme impact it may have on results of the resident species procedure. The FAV equation is designed so that the fewer available acute values, the more conservative the resulting FAV. When the resident species procedure is used for a chemical for which national WQC are based on a large number of species, the FAV equation will most likely produce a FAV that is overprotective compared to the national value. An overprotective criterion will also occur if the database has a preponderance of sensitive species rather than covering a broad range of species sensitivities.

The role of database size in the criteria development can be illustrated by considering the hypothetical situation in which the national database consists of only the nine most sensitive species instead of a total of 41. The resulting FAV would be  $13.4 \,\mu\text{g/L}$ , which is comparable to the value based on the Blaine Creek database ( $10.1 \,\mu\text{g/L}$ ) and approximately one-fourth lower than the value of  $18.5 \,\mu\text{g/L}$  based on a database size of 41. A similar result is evident using the Blaine Creek database. Using a database size of 33 (based on the recalculation procedure), the resulting FAV of  $36.3 \,\mu\text{g/L}$  is more than three times the FAV of  $10.1 \,\mu\text{g/L}$  based on a database of nine. The importance of database size is dependent on how close together the lowest four acute values in the database are, as they determine the slope of the line being used to extrapolate to the

FAV. The greater the distance between the values, the steeper the slope, and the more important database size is in determining the FAV.

Two distinctly different values were obtained using the procedures just discussed (i.e., resident species and recalculation procedures; Table 4) and can be explained by noting the large difference in cumulative probability values assigned to the most sensitive genus (*Daphnia*) using the different procedures (Table 5). Table 5 compares the lowest four acute values and their respective cumulative probabilities used to extrapolate to the FAV (cumulative probability 0.05) for the Blaine Creek database and the USEPA database modified by the recalculation procedure. It is important to remember that these values were used for a log GMAV-cumulative probability plot to obtain the FAV. Because of the effect of database size, the cumulative probability assigned to *Daphnia* is three times higher using the resident species compared to the recalculation procedure. When the database is small (<20 organisms), the FAV equation must extrapolate below the lowest acute value instead of estimating the 0.05 level based on surrounding records.

Results of copper speciation analyses below the discharge clearly indicate a site-water effect reducing the amount of bioavailable copper. The FAV and CMC computed by the recalculation procedure were multiplied by the geometric mean ratio of dissolved to total recoverable copper to adjust for this site water effect. Multiplying the CMC of  $31.2~\mu g/L$  (at a site hardness of 173~mg/L) by the speciation ratio of 0.58 results in a criterion of  $53.8~\mu g/L$ , which accounts for both site-water effects and species composition. It should be noted that it would be inappropriate to modify a criterion derived by either the resident or indicator species procedures by this method because they already account for site-water effects.

### **Conclusions**

Results of the acute toxicity tests for copper using Blaine Creek water are in general agreement with values reported by the USEPA (USEPA, 1984). However, use of the resident species procedure for Blaine Creek resulted in a proposed criterion that was overprotective when compared to national WQC for copper and other site-specific derivation procedures. Overprotection is mostly due to the effect of database size in the calculation process, rather than differences in the relative sensitivity of the test species. The FAV equation is justifiably designed to yield a more conservative criterion when a smaller database is used. For chemicals such as copper, for which a large database already exists, the resident species procedure has an inherent bias resulting in an unduly conservative value. A conservative bias is also introduced into the resident species procedure if the range of the test species contains a preponderance of sensitive organisms.

The recalculation procedure, as modified on the basis of metal bioavailability, appeared to be the most appropriate site-specific modification of the statewide or national criterion. It generated a less stringent FAV, and it was based on factors known to mitigate the toxicity of copper in aquatic environments. A higher criterion is supported by analysis of extensive data on biological monitoring at the site. In this particular case, the regulatory agency does not have to assume a conservative approach because the weight of evidence (biosurvey and chemical speciation data) supports a less stringent site-specific criterion.

The key to derive appropriate site-specific WQC is to focus on the chemical and biological factors that are most important at a specific site. Based on this research, use of the resident species procedure is not recommended unless the national WQC are derived from a small database. Use of the recalculation procedure, metal bioavailability information, the indicator

organism approach, or combination of these appears to be more appropriate and cost-effective techniques to derive site-specific criteria. Regulatory agencies should recognize that method flexibility and novel approaches are acceptable and can result in protective site-specific criteria.

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### **Estimated Costs to Conduct a Resident Species Study**

The determination of a site-specific criterion using the resident species approach is an expensive undertaking. A minimum of eight species representing the required families are needed to generate the site-specific criterion. Considerable time is needed to collect an appropriate number of resident organisms in the field and to develop holding and testing procedures that will produce acceptable results. Although in-house cultures or commercial suppliers can be used for obtaining resident species, it is anticipated at least half of the species used will be obtained from the site. The case study presented above used nine species, five of which were obtained from in-house or a commercial supplier and four were collected from the site. Since tests should be replicated to capture variability of the results, a minimum of 16 tests will be conducted during the study.

The estimated costs for a resident species study in which static or static-renewal acute tests are used to derive a site-specific criterion for a metal or metalloid can range from \$100,000 to \$200,000. Studies in which flow-through tests are used or studies in which the measurement of the chemical of interest is more costly than that for a metalloid will be more expensive.